(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) Publication number: **0 598 470 A2**

(12) EUROPEAN PATENT APPLICATION

(21) Application number: 93303089.2

(51) Int. Cl.^{5}: H02J 7/10

(22) Date of filing: 21.04.93

(30) Priority: 19.11.92 JP 335283/92
21.12.92 JP 339956/92

(43) Date of publication of application:
25.05.94 Bulletin 94/21

(84) Designated Contracting States:
DE FR GB IT

(71) Applicant: TOKIN CORPORATION
7-1, Koriyama 6-chome
Taihaku-ku
Sendai-shi Miyagi-ken 982(JP)

(72) Inventor: Momotani, Hiroshi, c/o Tokin Corporation
7-1, Koriyama 6-chome,
Taihaku-ku
Sendai-shi, Miyagi-ken(JP)
Inventor: Hasebe, Akio, c/o Tokin Corporation
7-1, Koriyama 6-chome,
Taihaku-ku
Sendai-shi, Miyagi-ken(JP)
Inventor: Otsuki, Etsuo, c/o Tokin Corporation
7-1, Koriyama 6-chome,
Taihaku-ku
Sendai-shi, Miyagi-ken(JP)
Inventor: Takeuchi, Tamiko, c/o Tokin Corporation
7-1, Koriyama 6-chome,
Taihaku-ku
Sendai-shi, Miyagi-ken(JP)

(74) Representative: Cropp, John Anthony David
MATHYS & SQUIRE
10 Fleet Street
London, EC4Y 1AY (GB)

(54) Method and apparatus for charging a secondary battery by supplying pulsed current as charging current.

(57) In a method for charging a secondary battery having a positive electrode, a negative electrode, and an electrolyte, a pulsed current is supplied to the secondary battery to make the pulsed current flow between the positive electrode and the negative electrode through the electolyte to thereby charge the secondary battery. The pulsed current suitably comprises positive pulse current which has a positive pulse amplitude corresponding to a first current density of 1 μA/cm^2 to 100 mA/cm^2 in the positive electrode. However, it may have negative pulse current each following after each positive pulse and having a negative amplitude corresponding to a second current density which preferably is not greater than a quarter of the first current density.

Background of the Invention:

The present invention relates to a method and an apparatus for charging a secondary battery.

Recently, electrical or electronic machines have been reduced in size and weight and have been made cordless, with development of electronics. The secondary battery, for example, a lithium (Li) secondary battery, a nickel-cadmium (Ni-Cd) battery, and a nickel-zinc (Ni-Zn) battery, or the like, is known and used as a power source of such electrical or electronic machines. Under the circumstances, it is strongly desired that the secondary battery has a long cycle life so that the secondary battery can be repeatedly charged and discharged many times.

The secondary battery generally comprises, as well known, a positive electrode, a negative electrode, and an electrolyte. The secondary battery is conventionally provided with a separator which separates the positive electrode and the negative electrode.

The secondary battery is conventionally charged by supplying an electric direct current (DC current). Accordingly, a conventional method for charging the secondary battery comprises the steps of producing a DC current, and supplying the DC current to the secondary battery to make the DC current flop from the positive electrode to the negative electrode through the electrolyte to thereby charge the secondary battery. Thus, it is cycled that the secondary battery is charged after being discharged, so that the secondary battery can be used for a long time.

It is known in the art that dendrite crystal grows on a surface of the negative electrode, when the secondary battery is charged. The growth of the dendrite crystal is accelerated, as the charging-discharging cycle is repeated many times. As a result, the grown dendrite crystal often breaks through the separator and comes into contact with the positive electrode, so that the positive electrode and the negative electrode are short-circuited. Eventually, the secondary battery becomes unusable.

Thus, the growth of the dendrite crystal makes the cycle life of the secondary battery short.

In case of the Li secondary battery, the short circuit between the positive electrode and the negative electrode often causes fire. Accordingly the growth of the dendrite crystal unfortunately brings the Li secondary battery into danger of catching fire.

When the Ni-Cd and the Ni-Zn batteries are rapidly charged by use of large DC current, those batteries rise in temperature by the Joule's heat due to an internal resistance of those batteries. The temperature rise inevitably deteriorates a charge acceptability on the positive electrode. As a result, the Ni-Cd and the Ni-Zn batteries are reduced in capacity.

The Ni-Cd battery suffers from another particular problem, what is called, a "memory effect". Namely, the Ni-Cd battery memorizes a residual discharging capacity when charging starts. After completion of charging, the Ni-Cd battery stops discharging at the memorized residual discharging capacity. Consequently, a dischargeable capacity of the Ni-Cd battery is considerably deteriorated, when charged before discharge is completed up to 100% of the discharging capacity.

It is unknown why the Ni-Cd battery suffers from the "memory effect". In order to protect the Ni-Cd battery from the "memory effect", charging of the Ni-Cd battery should strictly be restricted so that the Ni-Cd battery is charged only after the discharge has completely come up to 100%. Alternatively, a charging apparatus for use in charging the Ni-Cd battery is provided with a circuit which enables the Ni-Cd battery to be charged only after it has been discharged up to 100%.

Summary of the Invention:

It is therefore an object of this invention to provide a method of charging a secondary battery which enables the secondary battery to have a long cycle life.

It is another object of this invention to provide a method of the type described, which can prevent a Li secondary battery from catching fire.

It is still another object of this invention to provide a method of the type described, which can rapidly charge the secondary battery by use of large current.

It is further another object of this invention to provide a method of the type described, which can prevent a Ni-Cd battery from suffering from the "memory effect".

Other objects of this invention will become clear as the description proceeds.

According to an aspect of this invention, there is provided a method for charging a secondary battery which has a positive electrode, a negative electrode, and an electrolyte. The method comprises the steps of:

producing a pulsed current; and

supplying the pulsed current to the secondary battery to make the pulsed current flow between the

positive electrode and the negative electrode through the electrolyte to thereby charge the secondary battery.

According to another aspect of this invention, there is provided a charging apparatus for use in charging a secondary battery having a positive electrode, a negative electrode, and an electrolyte. The charging apparatus comprises:

DC power supply means for supplying a DC power with a constant current;

pulsed power generating means connected to the DC power supply means for generating a pulsed power from the DC power, the pulsed power being repeated with a controllable frequency, a controllable duty ratio, and a controllable waveform;

pulsed power control means connected to the pulsed power generating means for controlling the pulsed power to set the controllable frequency, the controllable duty ratio, and the controllable waveform into a predetermined frequency, a predetermined duty ratio, and a predetermined waveform; and

output port means coupled to the pulsed power generating means and to be connected with the secondary battery for supplying the pulsed power to the secondary battery to make a pulsed current flow between the positive electrode and the negative electrode through the electrolyte to thereby charge the secondary battery.

<u>Brief Description of the Drawing:</u>

Fig. 1 is a schematic sectional view of a known Li secondary battery;

Fig. 2 is a block diagram of a charging apparatus according to the present invention;

Fig. 3 is a graph for illustrating cycle life characteristics of Li secondary battery charged by different pulsed currents according to a first sample of this invention in comparison with a conventional charging method by use of DC current;

Figs. 4(a) and 4(b) show a couple of photos each showing microstructure of a surface of a negative electrode of Li secondary battery, Fig. 4(a) being after charged by a pulsed current, Fig. 4(b) being after charged by a DC current;

Fig. 5 is a graph illustrating cycle life characteristics of Li secondary battery charged by use of different pulsed current according to a second example of this invention in comparison with a conventional charging method by use of DC current;

Fig. 6 shows a waveform of a pulsed current which is used in a method according to a third example of this invention;

Figs. 7 and 8 are graphs illustrating cycle life characteristics of Li secondary battery charged according to the third example of this invention, numbers of curves corresponding to test numbers in Table 1;

Fig. 9 is a schematic sectional view of a known Ni-Cd battery;

Fig. 10 is a graph illustrating cycle life characteristics of Ni-Cd battery charged according to a fourth example of this invention, where the pulsed current is 18mA, in comparison with a conventional charging method by use of DC current of 18mA;

Fig. 11 is a graph illustrating cycle life characteristics of Ni-Cd battery charged according to the fourth example of this invention where the pulsed current is 180mA, in comparison with a conventional charging method by use of DC current of 180mA:

Fig. 12 is a graph illustrating a relation of capacity of each Ni-Cd battery in response to an amount of charged current according to a sixth example of this invention in comparison with a conventional charging method by use of DC current of 180mA:

Fig. 13 is a graph illustrating a relation of capacity of each Ni-Cd battery in response to the numbers of the cycle according to a seventh example of this invention, in comparison with a conventional charging method by use of DC current of 180mA:

Fig. 14 is a graph illustrating a relation of a temperature of a surface of the Ni-Cd battery in response to a charge capacity according to the seventh example of this invention, in comparison with a conventional charging method by use of DC current of 180mA;

Fig. 15 is a graph illustrating a relation of capacity of Ni-Cd battery in response to a thickness of the separator according to an eighth example of this invention;

Fig. 16 is a graph illustrating a relation of discharge voltage in response to a service capacity of Ni-Cd battery according to a ninth example, in comparison with a conventional charging method by use of DC current of 180mA;

Fig. 17 is a graph illustrating a relation of capacity deterioration rate of Ni-Cd battery in response to the numbers of the cycle according to a tenth example in comparison with a conventional charging method by use of DC current of 180mA;

Example 1

In order to estimate effects of the charging method of the present invention as to the cycle life characteristics of a lithium (Li) secondary battery, a charge-discharge cycle test was carried out for several samples of Li secondary battery.

In the Li secondary battery, the positive electrode is made of a manganese dioxide, while the negative electrode is made of lithium metal. The electrolyte is such a solution that a $LiClO_4$ is melted in propylene carbonate (PC) with a concentration of 1 N (normal).

In the charge-discharge cycle test, the charging operation was performed to charge each of samples to a charged voltage of 3.5 V by use of the charging apparatus shown in Fig. 2. The pulsed current used for charging was differently adjusted for different samples to have different pulse repetition frequencies of 100 Hz, 10 kHz, and 0.1 Hz and a constant pulse duty ratio of 50%. Each pulse of the pulsed current was also adjusted to have a constant positive pulse amplitude sufficient to make a current of 0.1 mA flow per 1 cm^2 of the positive electrode of the battery. That is, the positive pulse amplitude is corresponding to a current density of 0.1 mA/cm^2 in the positive electrode of the battery. Thus, the maximum current density flowing through the positive electrode is 0.1 mA/cm^2.

For comparison, one of the samples was charged to 3.5 V by use of a DC current having a positive level corresponding to a current density of 0.1 mA/cm^2 in the positive electrode of the battery.

The discharge was performed by continuously supplying a current from the charged sample to a load at a rate of a current density of 0.1 mA/cm^2 in the positive electrode until the battery voltage became 2.0 V. A time period was measured for the voltage of each sample battery dropped from 3.5 V to 2.0 V. A supplying current was also measured when the supplying voltage became 2.0 V. A discharging capacity of each sample battery after each charging operation was calculated from the measured time period and the supplying current.

Providing that an initial discharging capacity after an initial charging operation is 100%, variation of the discharging capacity after each charging operation is shown in Fig. 3 as a relation between numbers of charge-discharge cycle and a deterioration rate of the battery discharging capacity.

It is noted from Fig. 3 that the samples charged by use of a pulsed current according to the present invention are considerably low in deterioration of battery discharging capacity in comparison with the sample charged by use of DC current according to the conventional charging method.

In order to seek for the grounds that cycle life characteristics of the samples charged by the pulsed current are superior to those charged by the DC current, as suggested in Fig. 3, microstructure of a surface of a negative electrode of each one of the samples is observed by use of a scanning electron microscope (SEM). Fig. 4(a) shows the SEM photo of the sample charged by the pulsed current with the pulse repetition frequency of 10 kHz and the pulse amplitude corresponding to the current density of 0.1 mA/cm^2. Fig. 4(b) shows that of the sample charged by the DC current corresponding to the current density of 0.1 mA/cm^2.

It is noted from Figs. 4(a) and 4(b) that lithium has been deposited in a form of granules on the surface of the negative electrode of the sample charged by the pulsed current, while dendrite crystal has grown on the surface of the negative electrode of the sample charged by the DC current.

In view of results of the above charge-discharge cycle test and the SEM photos, it is readily understood that a growth of the dendrite crystal on a surface of a negative electrode causes a deterioration of cycle life characteristics and a short-circuit between a positive and a negative electrodes of a Li secondary battery.

Thus, the method according to the embodiment of the present invention can prevent the Li secondary battery from being deteriorated in the cycle life characteristics and short-circuited due to such a growth of the dendrite crystal.

Example 2

From different point of view, another charge-discharge cycle test was carried out for several samples of Li secondary battery which are experimentally produced by use of the similar materials to those of the samples in Example 1.

In the charge-discharge cycle test, the charging operation was performed to charge each of samples to a charged voltage of 3.5 V by use of the same charging apparatus as that used in Example 1. Each pulsed current used for charging was adjusted to have the constant pulse repetition frequency of 100 Hz and a pulse duty ratio of 50%. The pulse of the pulsed current was differently adjusted for different samples to have different positive pulse amplitudes which are corresponding to different current densities of 1 $\mu A/cm^2$, 0.1 mA/cm^2, 1 mA/cm^2, and 100 mA/cm^2 in the positive electrode of the battery.

The positive amplitude was, as described in Table 1, corresponding to first current densities of 1 $\mu A/cm^2$ to 1 x 10^5 $\mu A/cm^2$ (100 mA/cm^2) in positive electrodes in the test samples 1 to 7. The negative amplitude was corresponding to second current densities of 0.25 $\mu A/cm^2$ to 10 $\mu A/cm^2$ which are less than the first current density, as described in Table 1.

As described in Table 1, the pulsed current used for charging each of the test samples 1 to 5 was adjusted to have a constant pulse repetition frequency of 100 Hz and a constant pulse duty ratio of 50%. The pulsed current used for charging test samples 6 and 7 was adjusted to have pulse repetition frequencies of 0.1 Hz and 10 kHz, respectively, and the constant pulse duty ratio of 50%.

The charging and the discharging operations were performed in the similar manner to that in Examples 1 and 2, as will be understood in Table 1.

For comparison, one of the samples was charged to 3.5 V by use of DC current having a positive level corresponding to a current density of 0.1 mA/cm^2 in the positive electrode of the battery.

Results of the charge-discharge cycle tests are shown in Figs. 7 and 8. Fig. 7 shows a result of test samples 1 to 5 which were charged by use of pulsed currents having the same pulse repetition frequency but different positive and negative pulse amplitudes. Fig. 8 shows a result of test samples 3, 6, and 7 which were charged by use of pulsed currents having different pulse repetition frequencies but the same positive and negative pulse amplitudes.

It is noted from Figs. 7 and 8 that the samples charged by use of the pulsed current according to the present Example are very low in deterioration of battery discharging capacity in comparison with the sample charged by use of DC current according to the conventional charging method.

Preferably, the aforesaid second current density should not be greater than a quarter of the aforesaid first current density so as not to elongate a charging time period.

Example 4

In this Example, ten samples of sealed Ni-Cd secondary battery were experimentally produced, one of which is illustrated in Fig. 9.

Since the illustrated sample of Ni-Cd battery has similar structure to the secondary battery illustrated in Fig. 1, description for the structure of the Ni-Cd battery is omitted. Similar portions are designated by like reference numerals.

In the Ni-Cd battery, the positive electrode 34 is made of sintered nickel consisting substantially of nickel hydroxide, while the negative electrode 35 is made of paste cadmium consisting substantially of cadmium hydroxide. The electrolyte is such a solution as consisting substantially of kalium hydroxide. The separator 36 is made of nylon nonwoven fabric cloth.

In order to estimate effect of the charging method of the present invention to the cycle life characteristics of the Ni-Cd secondary battery, a battery discharging capacity test as well as a charge-discharge cycle test were carried out for the samples of Ni-Cd secondary battery.

In the tests, the pulsed current used for charging was adjusted for test samples 1 to 5 to be 180 mA and to have different pulse repetition frequencies of 1 Hz, 100 Hz, 5 kHz, 500 kHz, and 10 MHz with the same pulse duty ratio of 50%. Initially, those test samples 1 to 5 were charged up to 100% of its charging capacity with a current of 180 mA at a temperature of 20°C. It was cycled fifty times that the test samples 1 to 5 were charged up to 100% each after discharged up to a depth of discharge of 50% (for two and a half hours).

The pulsed current used for charging was adjusted for test samples 6 to 8 to be 18 mA and to have different pulse repetition frequencies of 1 Hz, 5 kHz, and 10 MHz with the same pulse duty ratio of 50%. Initially, those test samples 6 to 8 were charged up to 100% of its charging capacity with a current of 18 mA at a temperature of 20°C. It was also cycled fifty times that test samples 6 to 8 were charged up to 100% each after discharged up to a depth of discharge of 50% (for two and a half hours).

For comparison, two of test samples 9 and 10 were charged by use of a DC current of 180 mA and 18 mA, respectively. It was also cycled fifty times that test samples 9 and 10 were charged up to 100% each after discharged up to a depth of discharge of 50% (for two and a half hours).

Results of the tests are shown in the following Table 2 and Figs. 10 and 11.

Table 2

	PULSED CURRENT CHARGING CONDITION			INITIAL CAPACITY (mAh)	CAPACITY AFTER 50 CYCLES (mAh)	DETERIORATION RATE OF CAPACITY (%)
	PULSE REPETITION FREQUENCY (kHz)	DUTY RATIO (%)	CHARGE CURRENT (mA)			
Test Sample 1	0.001	50	180	210	191	91.0
Test Sample 2	0.1	50	180	202	195	96.5
Test Sample 3	5	50	180	217	208	95.9
Test Sample 4	500	50	180	203	195	96.1
Test Sample 5	10000	50	180	197	182	92.4
Test Sample 6	0.001	50	18	206	184	89.3
Test Sample 7	5	50	18	200	188	94.0
Test Sample 8	10000	50	18	209	188	90.0
	CURRENT		CHARGE CURRENT (mA)	INITIAL CAPACITY (mAh)	CAPACITY AFTER 50 CYCLES (mAh)	DETERIORATION RATE OF CAPACITY (%)
Test Sample 9	DC CURRENT		180	215	152	70.7
Test Sample 10	DC CURRENT		18	213	93	43.7

In Table 2, there are shown an initial discharging capacity, discharging capacity after the above-mentioned cycle of fifty times, and a deterioration rate of the battery discharging capacity. In Figs. 10 and 11, there are shown a relation of capacity deterioration rate of each sample in response to the numbers of the cycle.

It is noted from Table 2 and Figs. 10 and 11 that the samples charged by use of a pulsed current according to the present Example are very low in deterioration of battery discharging capacity in comparison with the sample charged by use of DC current according to the conventional charging method.

Example 5

In this Example, samples of sealed Ni-Cd secondary battery were produced, each of which was similar to that in Example 4.

From different point of view, a battery discharging capacity test as well as a charge-discharge cycle test were carried out for the samples, like in Example 4.

In the tests, the pulsed current used for charging was adjusted for samples 1 to 4 to be 180 mA and to have a pulse repetition frequency of 5 kHz with different pulse duty ratios of 10%, 25%, 50%, and 75%, respectively.

In addition, the initial condition and the discharging condition are similar to those of Example 4.

Results of the tests are shown in the following Table 3.

Table 3

PULSED CURRENT CHARGING CONDITION				INITIAL CAPACITY (mAh)	CAPACITY AFTER 50 CYCLES (mAh)	DETERIORATION RATE OF CAPACITY (%)
	PULSE REPETITION FREQUENCY (kHz)	DUTY RATIO (%)	CHARGE CURRENT (mA)			
Test Sample 1	5	10	180	207	201	97.1
Test Sample 2	5	25	180	211	203	96.2
Test Sample 3	5	50	180	200	186	93.0
Test Sample 4	5	75	80	204	185	90.7

It is noted from Table 3 that the samples charged by use of a pulsed current according to the present Example are very low in deterioration of battery discharging capacity, so that a pulse duty ratio is not related to the effect of the present invention.

Example 6

In this Example, several samples of sealed Ni-Cd secondary battery were experimentally produced, which had similar structures to those in Example 4. Each separator of the samples in this Example had a thickness of 0.25mm.

A comparison test for a discharging capacity as well as a charge-discharge cycle characteristic of the battery was carried out for the samples of Ni-Cd secondary battery.

In the test, the pulsed current used for charging was adjusted to be 18 mA to 720 mA for different samples and to have a constant pulse repetition frequency of 500 Hz with a constant pulse duty ratio of 50%.

It was cycled ten times that the samples were discharged up to 100% with a current of 36 mA after charged up to 100% with the pulsed current of 18 mA to 720 mA, respectively.

For comparison, the samples were charged by use of different DC current of 18 mA to about 200 mA. It was also cycled ten times on the same condition as the above.

A result of the test is shown in Fig. 12 by illustrating a relation of capacity of the samples in response to the charge current.

It is noted from Fig. 12 that the capacity of the samples charged by a pulsed current according to the method of the present invention are kept stable, even though the charge current increases. However, samples charged by use of a DC current according to the conventional method is considerably deteriorated in the capacity, as the charge current increases.

Example 7

In this Example, several samples of sealed Ni-Cd secondary battery were experimentally produced, which had the similar structures to those in Example 6

Like in Example 6, a comparison test was carried out on the conditions similar to those in Example 6, except that the pulsed current used for charging was adjusted to be 36 mA, 180 mA, and 540 mA for different samples 1 to 3 and that the DC current was adjusted to be 18 mA, 36 mA, and 180 mA for different samples 4 to 6.

A result of the test is shown in Fig. 13 by illustrating a relation of capacity of the samples in response to the numbers of the cycle.

It is noted from Fig. 13 that the capacity of the samples charged by a pulsed current according to the method of the present invention are kept stable even though the charge current becomes large in comparison with the ones charged by use of a DC current according to the conventional method. It is also noted from Fig. 13 that the capacity of the samples charged by a pulsed current according to the method of the present invention are kept stable even though the numbers of the cycle increase.

Further, another result of the test is shown in Fig. 14 by illustrating a relation of a temperature of a battery surface in response to the charge current.

It is noted from Fig. 14 that the temperature of the battery surface of the samples 1 to 3 charged by a pulsed current according to the method of the present invention are kept stable, even though the charge current increases. However, the temperature of the battery surface of the samples 4 to 6 charged by use of a DC current according to the conventional method rises, particularly in the sample 6, as the charge current increases.

Thus, according to the method of the present invention, the Ni-Cd secondary battery can be rapidly charged by use of large current. Furthermore, if charged by use of such a large current, the Ni-Cd secondary battery can be prevented from temperature rise, so that it is not reduced in capacity.

Example 8

In this Example, first, a sample of sealed Ni-Cd secondary battery were produced, which had the thickness of the separator of 0.25 mm similar to that of the Example 7.

Second, several samples of the Ni-Cd secondary battery were experimentally produced which had different separators of 0.225mm, 0.2mm, and 0.175mm in thickness. The volume of the positive electrode of each sample was increased in correspondence to the decrease in thickness of each separator.

A battery capacity test was carried out for each sample mentioned above.

In the test, the pulsed current used for charging was adjusted to be 36 mA and to have a pulse repetition frequency of 500 Hz with a pulse duty ratio of 50%. The samples were discharged up to 100% with a current of 36 mA after charged up to 100% with the above pulsed current.

A result of the test is shown in Fig. 15 by illustrating a relation of capacity of each sample in response to a thickness of the separator of each sample.

It is noted from Fig. 15 that the capacity of the each sample is increased corresponding to the decrease in thickness of the separator of each sample.

Example 9

In this Example, two samples of sealed Ni-Cd secondary battery were produced in the manner similar to that of Example 6, one of which had a thickness of the separator of 0.175mm, and another of which had a thickness of 0.25mm.

A battery capacity test was carried out for the two samples by measuring a discharge after charged by a pulsed current of the conditions similar to those of the Example 8.

A result of the test is shown in Fig. 16 by illustrating a relation of discharge voltage of each sample in response to discharging capacity.

It is noted from Fig. 16 that the discharging capacity of the Ni-Cd secondary battery is increased when a separator of the Ni-Cd secondary battery is decreased in thickness.

Example 10

In this Example, two samples of sealed Ni-Cd secondary battery were produced in similar manner to that of Example 6, both of which had a thickness of the separator of 0.175mm.

A battery capacity test was carried out for the two samples. In the test, it was cycled that one of the test samples wad discharged up to 100% with a current of 36 mA after charged up to 100% by a pulsed current adjusted to be 36 mA and to have a pulse repetition frequency of 500 Hz with a pulse duty ratio of 50%. It was also cycled that another one of the test samples was discharged up to 100% with a current of 18 mA after charged up to 100% by a DC current adjusted to be 18 mA.

A result of the test is shown in Fig. 17 by illustrating a relation of deterioration rate of capacity of each sample in response to the numbers of the cycles.

It is noted from Fig. 17 that a cycle life characteristic of the Ni-Cd battery is not so deteriorated even though a separator of the Ni-Cd battery has a decreased thickness of 0.175mm, when the Ni-Cd battery is charged by a pulsed current according to the method of the present invention. In comparison with this, it is deteriorated in charging by use of DC current.

Thus, according to the method of the present invention, there can be provided a Ni-Cd secondary battery which has a separator having a thickness not greater than 0.25mm. Accordingly, a Ni-Cd secondary battery with a large capacity and a long cycle life is able to be provided.

Example 11

In this Example, several samples of sealed Ni-Zn secondary battery were experimentally produced.

Since the samples of Ni-Zn battery have similar structures to the secondary battery illustrated in Fig. 1, description for the structure of the Ni-Zn battery is omitted.

In the Ni-Zn battery, the positive electrode is made of sintered nickel consisting substantially of nickel hydroxide, while the negative electrode is made of zinc. The electrolyte is such a solution as consisting substantially of kalium hydroxide.

In order to estimate effect of the charging method of the present invention to the cycle life characteristic of the Ni-Zn secondary battery, a battery discharging capacity test as well as a charge-discharge cycle test were carried out for the samples of Ni-Zn secondary battery.

In the tests, the pulsed current used for charging was differently adjusted for different test samples 1 to 4 to have different pulse repetition frequencies of 1 Hz, 100 Hz, 10 kHz, and 10 MHz with a constant pulse duty ratio of 50%.

It was cycled that the best samples 1 to 4 were discharged up to 100% with a current of 200 mA each after charged up to 100% with the above-mentioned pulsed current of 80 mA.

For comparison, another test sample 5 was charged by use of a DC current of 80 mA. It was also cycled that test sample 5 was discharged up to 100% with a current of 200 mA after charged up to 100% with the DC current of 80 mA.

A result of the test is shown in Fig. 18 by illustrating a relation of deterioration rate of capacity of each sample in response to numbers of the cycle.

It is noted from Fig. 18 that a cycle life characteristic of test samples 1 to 4 is not so deteriorated even though numbers of the cycle increase. However, a cycle life characteristic of test sample 5 is drastically deteriorated, as numbers of the cycle increase.

Example 12

In this Example, several samples of sealed Ni-Zn secondary battery were experimentally produced, which had similar structures to those in Example 11.

A comparison test for a discharging capacity as well as a charge-discharge cycle characteristic of the battery was carried out for the samples of Ni-Zn secondary battery.

In the test, the pulsed current used for charging was differently adjusted for different samples to be 40 mA, 80 mA, 160 mA, and 320 mA and to have a constant pulse repetition frequency of 50 Hz with a constant pulse duty ratio of 50%.

It was cycled that the samples were discharged up to 100% with a current of 200 mA after charged up to 100% with the pulsed current of 40 mA, 80 mA, 160 mA, and 320 mA, respectively.

For comparison, the samples were charged by use of DC current differently adjusted for different samples to be 40 mA, 80 mA, and 160 mA. It was also cycled that the samples were discharged up to 100% with a current of 200 mA after charged up to 100% with the DC current of 40 mA, 80 mA, and 160 mA, respectively.

A result of the test is shown in Fig. 19 by illustrating a relation of numbers of the cycles in the samples in response to the charge current.

It is noted from Fig. 19 that the cycle life characteristics of the samples charged by the pulsed current according to the method of the present invention are not so deteriorated, even though the charge current increases. However, samples charged by use of the DC current according to the conventional method is considerably deteriorated in the cycle life characteristics, as the charge current increases.

It is also noted from Fig. 19 that the cycle life characteristics of the samples charged by the pulsed current are not so deteriorated, even though a large charge current, such as 160 mA or 320 mA, so that a Ni-Zn secondary battery can be rapidly charged according to the method of the present invention.

Example 13

In this Example, two samples of sealed Ni-Zn secondary battery were experimentally produced, which had similar structures to those in Example 11.

In order to seek for the grounds that cycle life characteristics or battery capacity of the Ni-Zn secondary battery charged by the pulsed current are superior to those charged by the DC current, a comparison test was carried out for the two samples of sealed Ni-Zn secondary battery.

In the test, the pulsed current used for charging was adjusted for one sample to have a pulse repetition frequency of 50 Hz with a pulse duty ratio of 50%. It was cycled that the test sample was discharged up to 100% with a current of 200 mA after charged up to 100% with the above-mentioned pulsed current of 80 mA. For comparison, another test sample was charged by use of a DC current of 80 mA. It was also cycled that the test sample was discharged up to 100% with a current of 200 mA after charged up to 100% with the DC current of 80 mA.

Then, microstructure of a surface of a negative electrode of each sample was observed by use of a scanning electron microscope (SEM). Fig. 20(a) shows the SEM photo of the sample charged by the pulsed current. Fig. 20(b) shows that of the sample charged by the DC current.

It is noted from Figs. 20(a) and 20(b) that typical zinc crystal has been deposited on the surface of the negative electrode of the sample charged by the pulsed current, while dendrite crystal has grown on the surface of the negative electrode of the sample charged by the DC current.

In view of the results of the above-mentioned comparison tests in Examples 11 and 12 and the SEM photos in Example 13, it is readily understood that a growth of the dendrite crystal on a surface of a negative electrode causes a deterioration of cycle life characteristics in the Ni-Zn secondary battery.

Thus, the method according to the present invention can prevent the Ni-Zn secondary battery from being deteriorated in the cycle life characteristics and short-circuited due to such a growth of the dendrite crystal. Furthermore, there can be provided a Ni-Zn secondary battery which is able to be rapidly charged, according to the present invention.

While this invention has thus far been described with respect to only several embodiments thereof, it will be readily possible for those skilled in the art to put this invention into practice in various other manners. For example, the pulsed current is not limited to a pulse current as illustrated in Fig. 6. Namely, a word "pulsed current" in the instant specification may include such a current as having a sinusoidal waveform, such a current as having a sawtooth waveform, and the like. Moreover, the charging apparatus illustrated in Fig. 2 must not be used to supply the pulsed current to the secondary battery. Alternatively, a half-wave rectified current may be supplied to the secondary battery by use of an AC power source and a rectifier.

Claims

1. A method for charging a secondary battery comprising a positive electrode, a negative electrode, and an electrolyte, said method comprising the steps of:
   producing a pulsed current; and
   supplying said pulsed current to said secondary battery to make the pulsed current flow between said positive electrode and said negative electrode through said electrolyte to thereby charge said secondary battery.

2. A method as claimed in Claim 1, said negative electrode being made of lithium, wherein said pulsed current has a predetermined repetition frequency which is between 0.1 Hz and 10 kHz, both inclusive, said pulsed current having a positive pulse amplitude which is corresponding to a predetermined current density of 1 $\mu A/cm^2$ to $100 mA/cm^2$, both inclusive in said positive electrode.

3. A method as claimed in Claim 1, said negative electrode being made of cadmium, said positive electrode being made of sintered nickel consisting substantially of nickel hydroxide, wherein said pulsed current has a predetermined repetition frequency which is between 1 Hz and 10 MHz, both inclusive, said pulsed current having a positive pulse amplitude which is corresponding to a predetermined current density of 1 $\mu A/cm^2$ to 100 mA/cm^2, both inclusive in said positive electrode.

4. A method as claimed in Claim 1, said negative electrode comprising zinc, said positive electrode comprising nickel, wherein said pulsed current has a predetermined repetition frequency which is between 1 Hz and 10 MHz, both inclusive, said pulsed current having a positive pulse amplitude which is corresponding to a predetermined current density of 1 $\mu A/cm^2$ to 100 mA/cm^2, both inclusive in said positive electrode.

5. A method as claimed in Claim 2, wherein said pulsed current comprises a positive pulsed current and a negative pulsed current following thereto which are repeated, said positive pulsed current having a positive amplitude which is corresponding to a first current density of 1 $\mu A/cm^2$ to 100 mA/cm^2 in said positive electrode, said negative pulsed current having a negative amplitude which is corresponding to

a second current density less than said first current density.

6. A method as claimed in Claim 5, wherein said second current density is not greater than a quarter of said first current density.

7. A charging apparatus for use in charging a secondary battery having a positive electrode, a negative electrode, and an electrolyte, said charging apparatus comprising:

DC power supply means for supplying a DC power with a constant current;

pulsed power generating means connected to said DC power supply means for generating a pulsed power from said DC power, said pulsed power being repeated with a controllable frequency, a controllable duty ratio, and a controllable waveform;

pulsed power control means connected to said pulsed power generating means for controlling said pulsed power to set said controllable frequency, said controllable duty ratio, and said controllable waveform into a predetermined frequency, a predetermined duty ratio, and a predetermined waveform; and

output port means coupled to said pulsed power generating means and to be connected with said secondary battery for supplying said pulsed power to said secondary battery to make a pulsed current flow between said positive electrode and said negative electrode through said electrolyte to thereby charge said secondary battery.

8. A secondary battery charged by a method as claimed in Claim 1, wherein said secondary battery comprises a separator separating said positive electrode and said negative electrode, said separator having a thickness not greater than 0.25mm.

9. A combination of a secondary battery and a charging apparatus, said secondary battery comprising a positive electrode, a negative electrode, and an electrolyte, said charging apparatus comprising:

DC power supply means for supplying a DC power with a constant current;

pulsed power generating means connected to said DC power supply means for generating a pulsed power from said DC power, said pulsed power being repeated with a controllable frequency, a controllable duty ratio, and a controllable waveform;

pulsed power control means connected to said pulsed power generating means for controlling said pulsed power to set said controllable frequency, said controllable duty ratio, and said controllable waveform into a predetermined frequency, a predetermined duty ratio, and a predetermined waveform; and

output port means coupled to said pulsed power generating means and to be connected with said secondary battery for supplying said pulsed power to said secondary battery to make a pulsed current flow between said positive electrode and said negative electrode through said electrolyte to thereby charge said secondary battery.

10. A combination of a secondary battery and a charging apparatus as claimed in Claim 9, wherein said secondary battery has a separator separating said positive electrode and said negative electrode, said separator having a thickness not greater than 0.25mm.

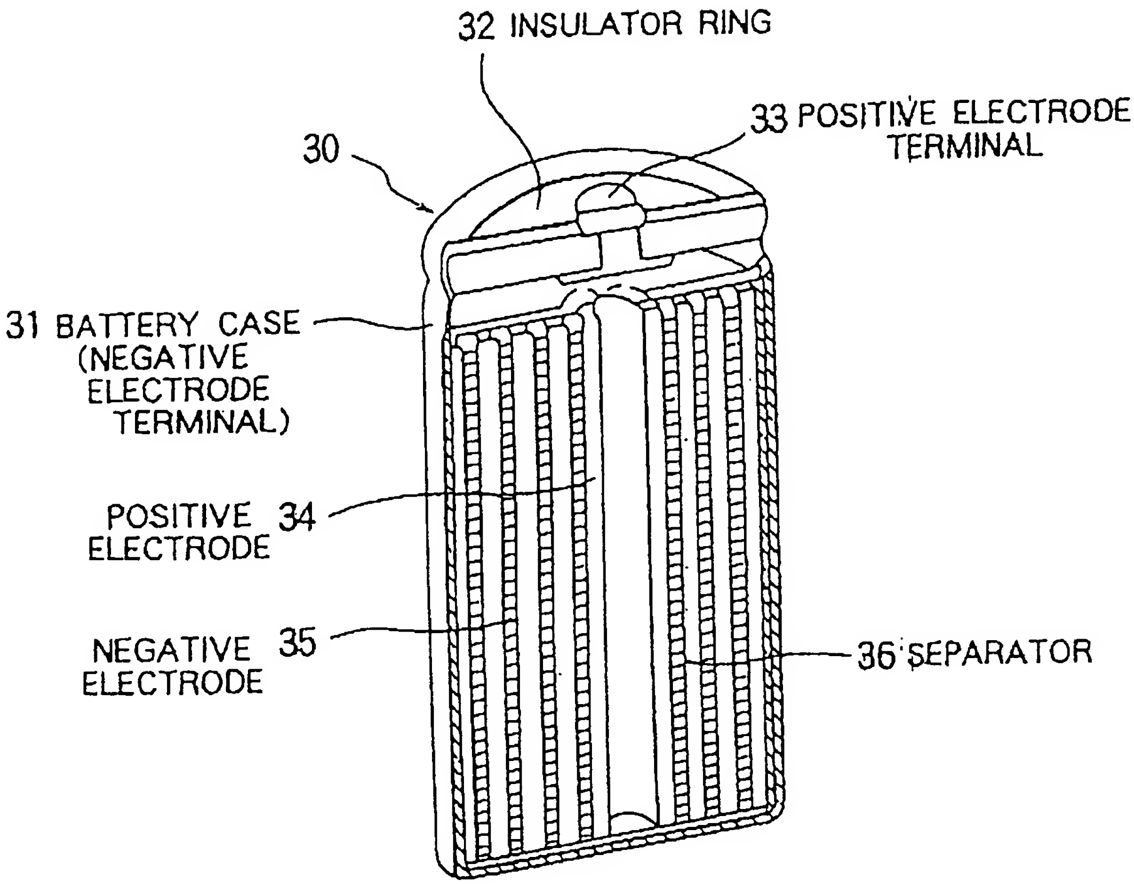

32 INSULATOR RING
33 POSITIVE ELECTRODE TERMINAL
30
31 BATTERY CASE (NEGATIVE ELECTRODE TERMINAL)
POSITIVE ELECTRODE 34
NEGATIVE ELECTRODE 35
36 SEPARATOR

FIG. 1

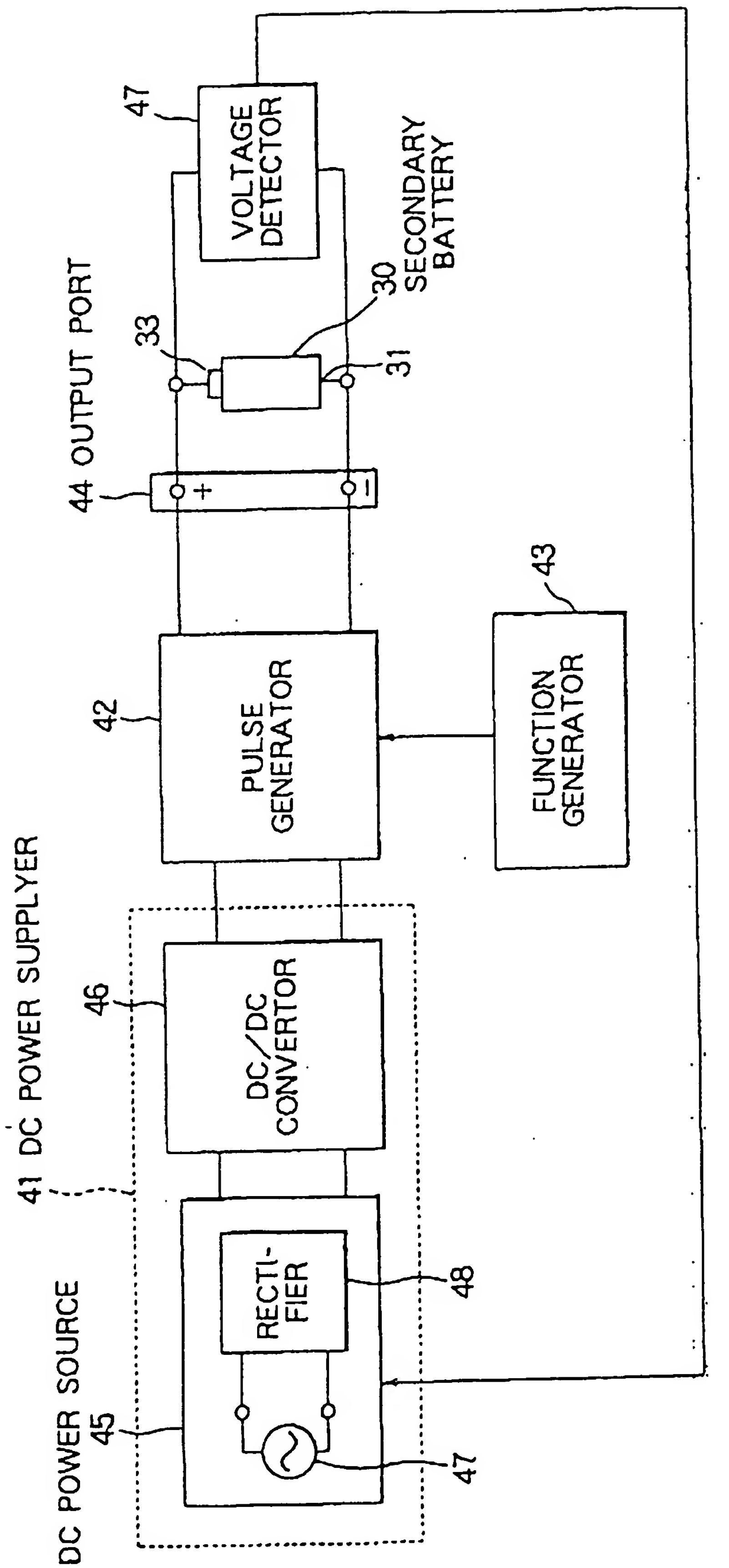

DC POWER SOURCE
45
41 DC POWER SUPPLYER
46
DC/DC CONVERTOR
RECTI-FIER
48
47
42
PULSE GENERATOR
43
FUNCTION GENERATOR
44 OUTPUT PORT
+
−
33
31
30
SECONDARY BATTERY
47
VOLTAGE DETECTOR

FIG. 2

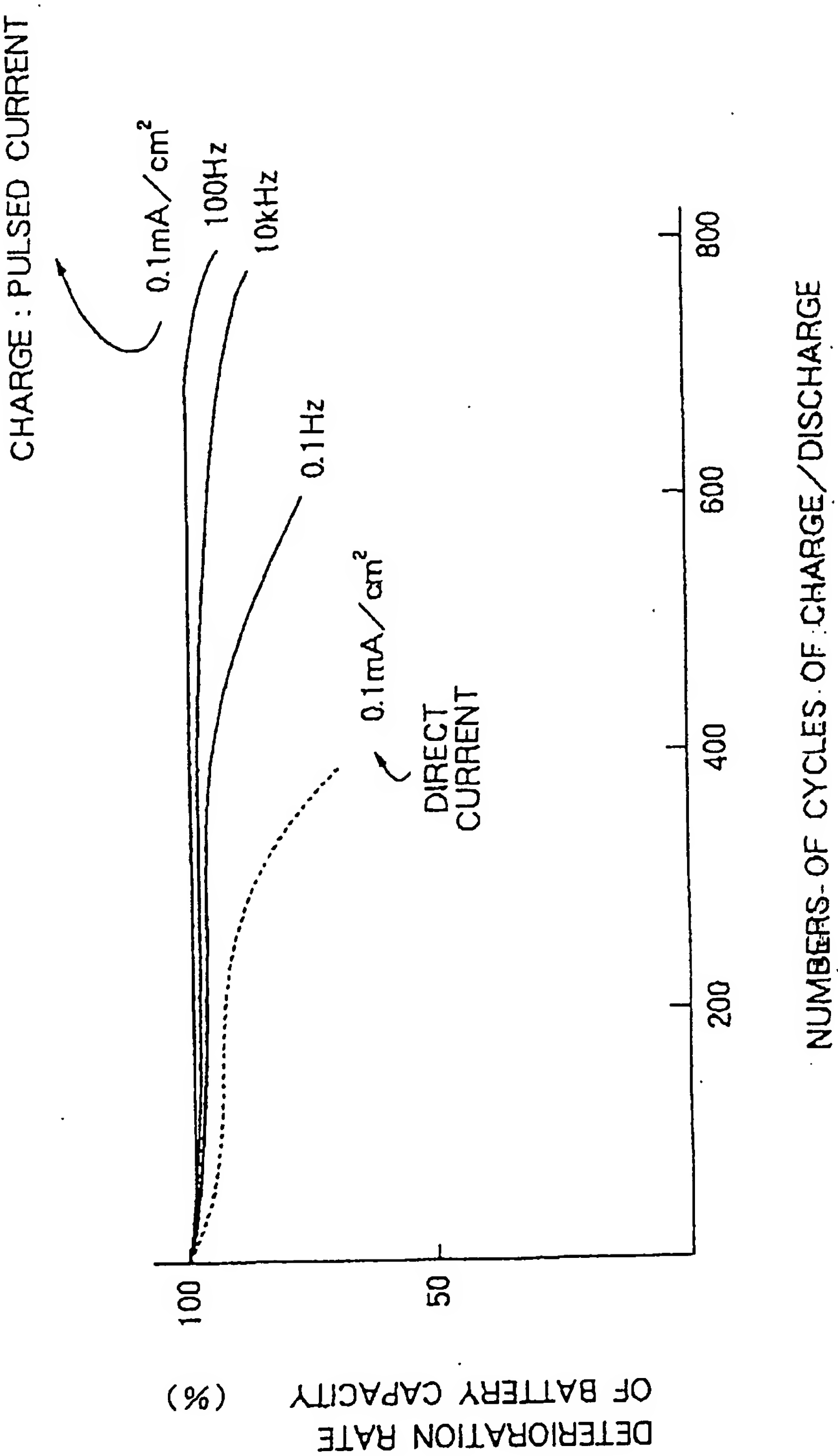

CHARGE : PULSED CURRENT
0.1mA/cm²
100Hz
10kHz
0.1Hz
0.1mA/cm²
DIRECT CURRENT
100
50
200
400
600
800
NUMBERS OF CYCLES OF CHARGE/DISCHARGE
DETERIORATION RATE OF BATTERY CAPACITY (%)

FIG. 3

B

(1)

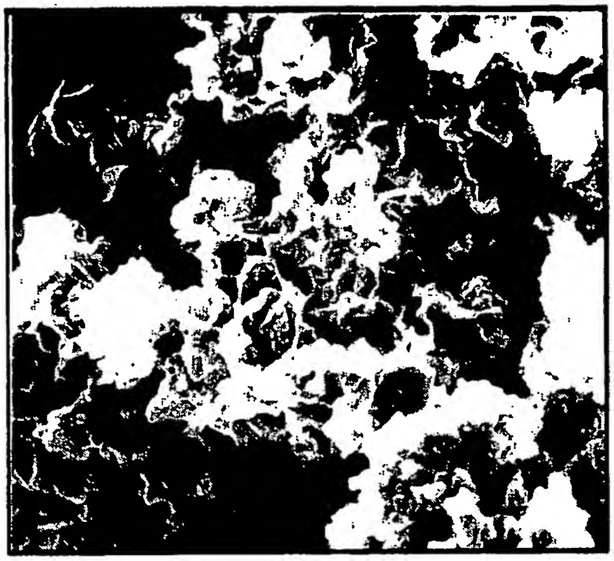


FIG.4(a)

20µm

(2)

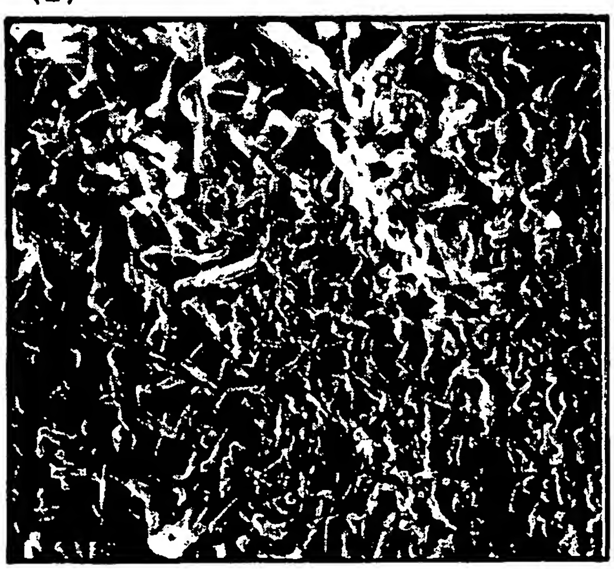
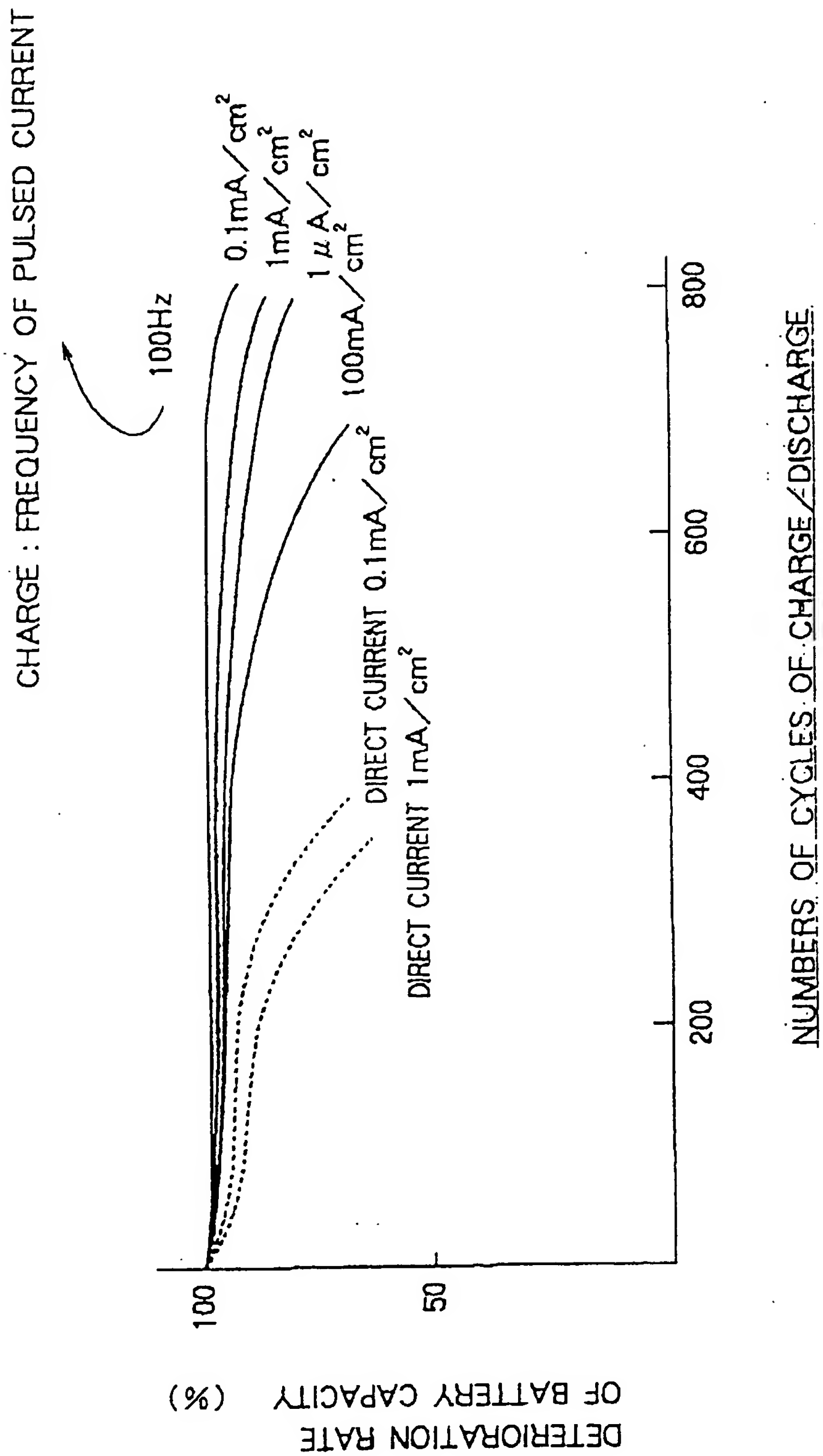


FIG.4(b)

20µm



CHARGE : FREQUENCY OF PULSED CURRENT
100Hz
0.1mA/cm2
1mA/cm2
1 μA/cm2
100mA/cm2
DIRECT CURRENT 0.1mA/cm2
DIRECT CURRENT 1mA/cm2
100
50
200
400
600
800
NUMBERS OF CYCLES OF CHARGE/DISCHARGE
DETERIORATION RATE OF BATTERY CAPACITY (%)

FIG. 5

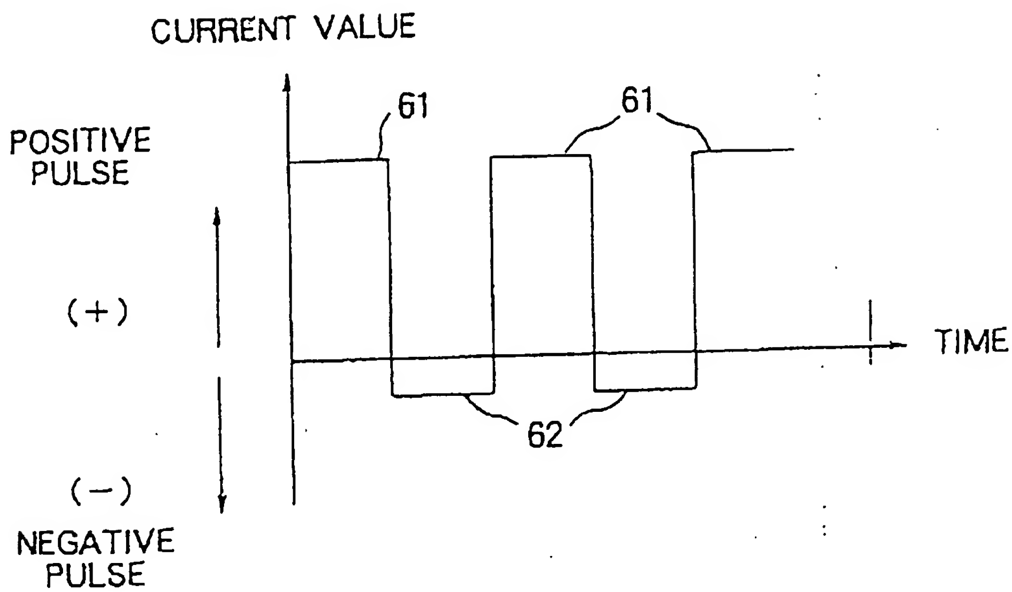


FIG. 6

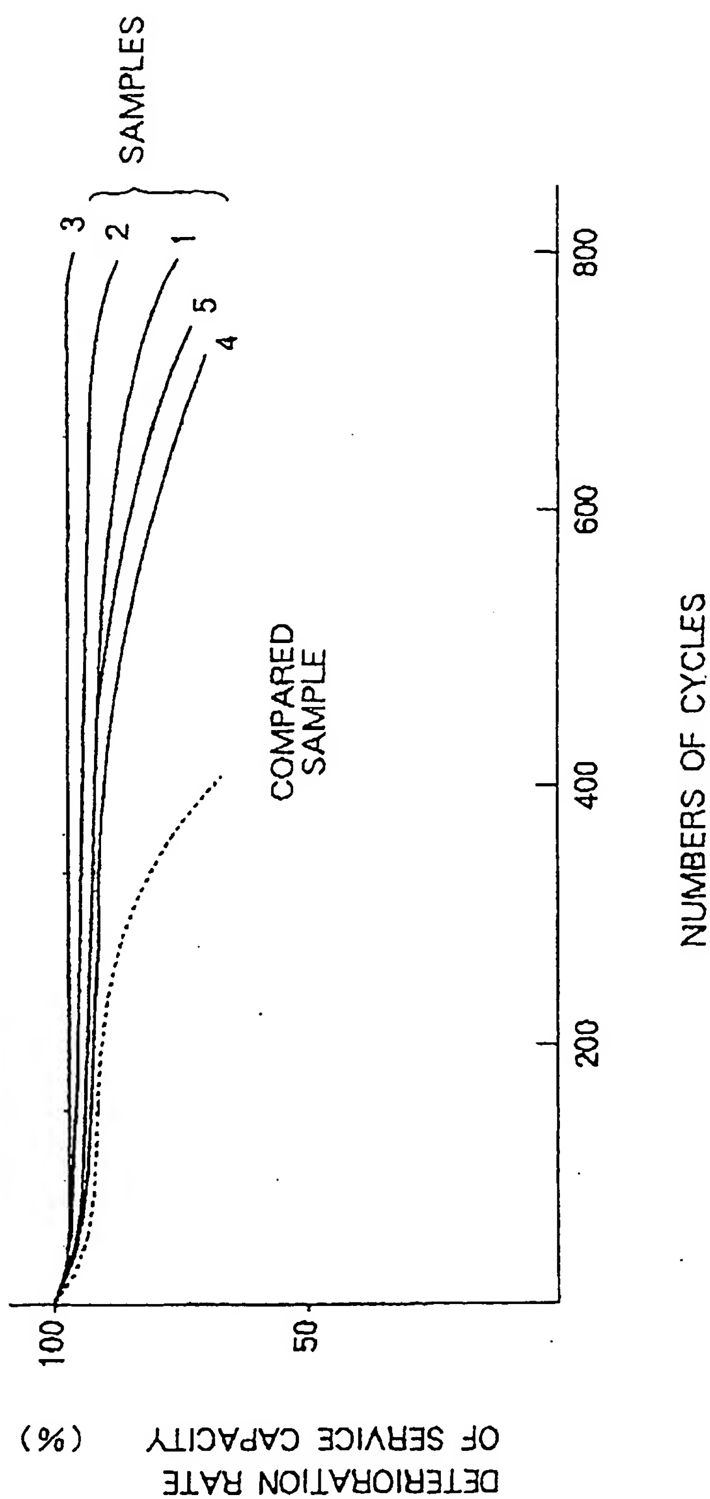

SAMPLES
3
2
1
5
4
COMPARED SAMPLE
100
50
200
400
600
800
NUMBERS OF CYCLES
DETERIORATION RATE OF SERVICE CAPACITY (%)

FIG. 7

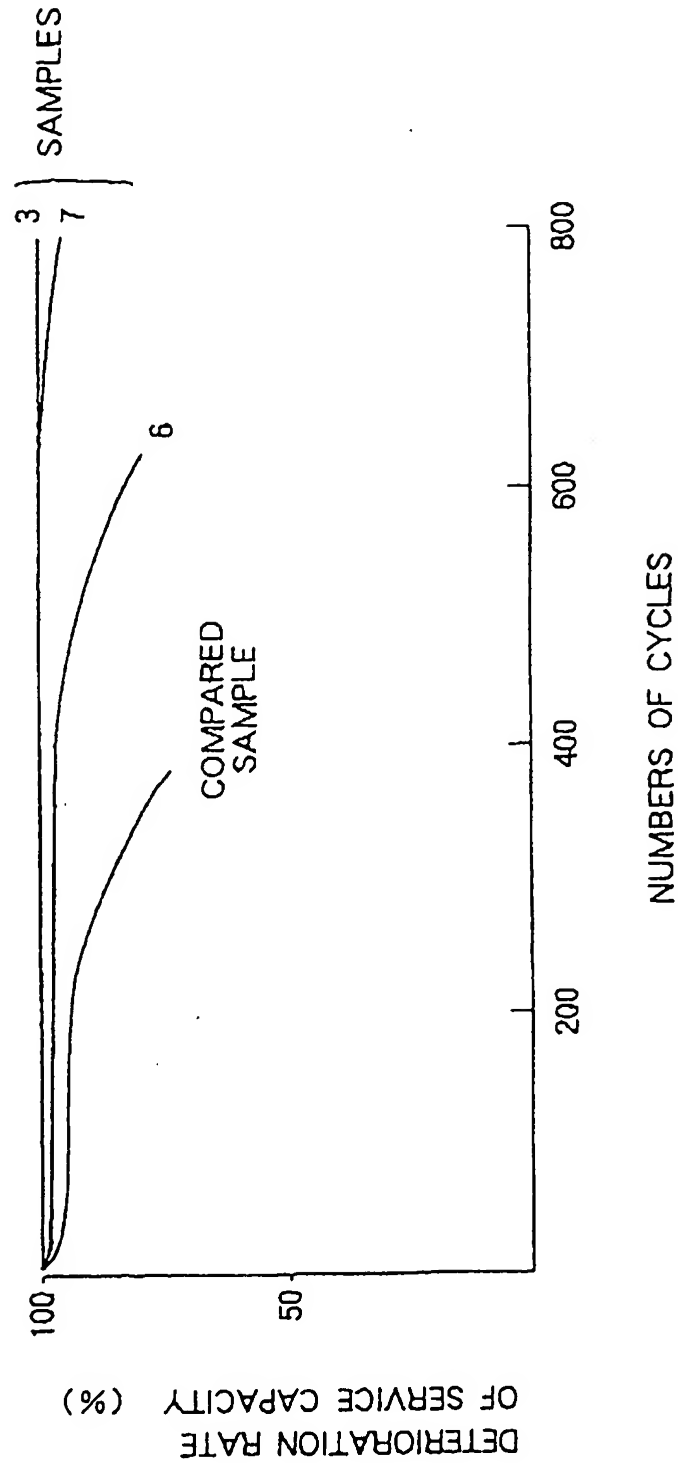

SAMPLES
3
7
6
COMPARED SAMPLE
100
50
200
400
600
800
NUMBERS OF CYCLES
DETERIORATION RATE OF SERVICE CAPACITY (%)

FIG. 8

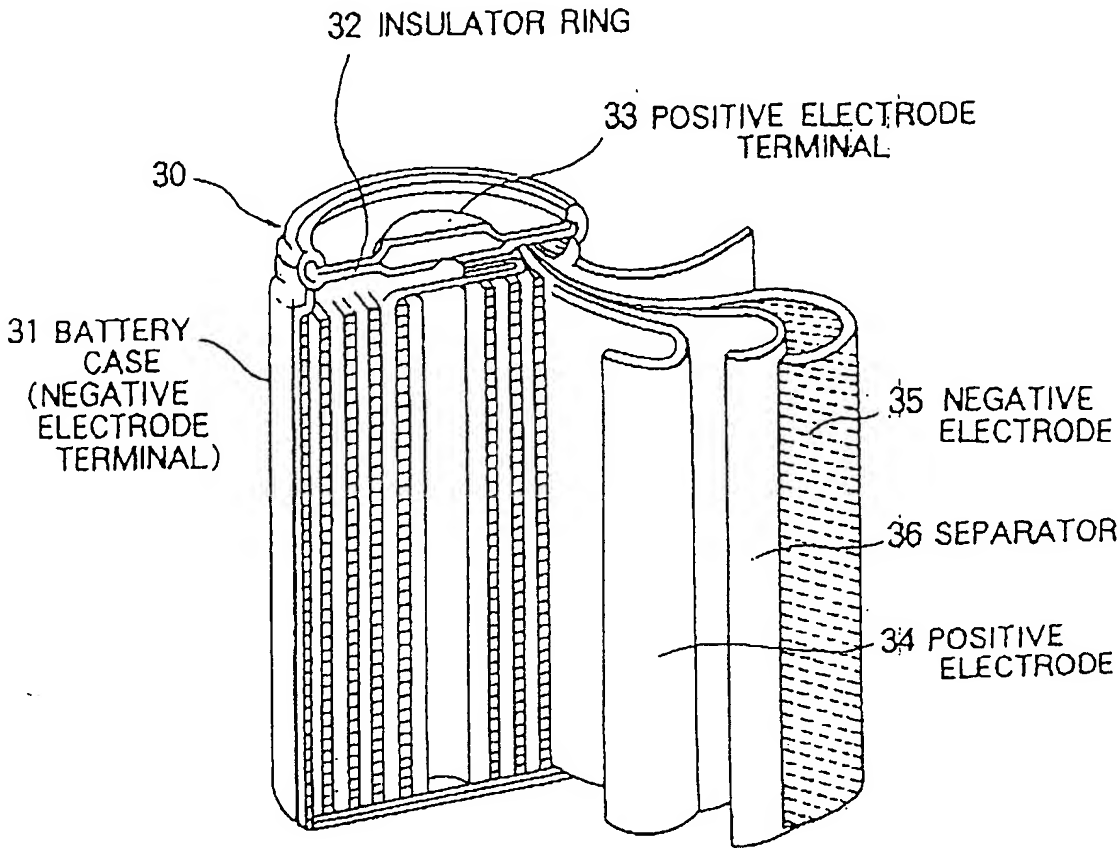
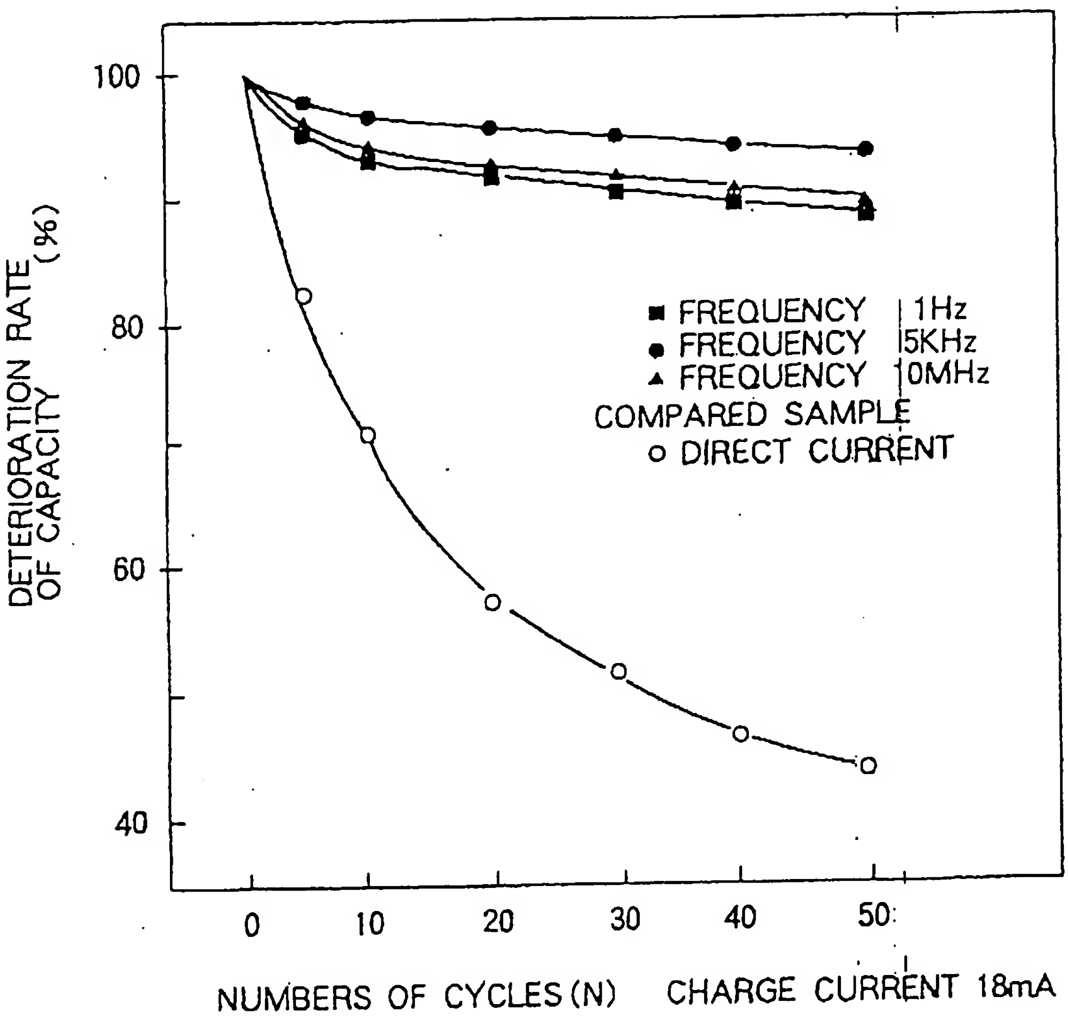

32 INSULATOR RING
33 POSITIVE ELECTRODE TERMINAL
30
31 BATTERY CASE (NEGATIVE ELECTRODE TERMINAL)
35 NEGATIVE ELECTRODE
36 SEPARATOR
34 POSITIVE ELECTRODE

FIG. 9



DETERIORATION RATE OF CAPACITY (%)
100
80
60
40
0
10
20
30
40
50
NUMBERS OF CYCLES (N)
CHARGE CURRENT 18mA
FREQUENCY 1Hz
FREQUENCY 5KHz
FREQUENCY 10MHz
COMPARED SAMPLE
DIRECT CURRENT

FIG. 10

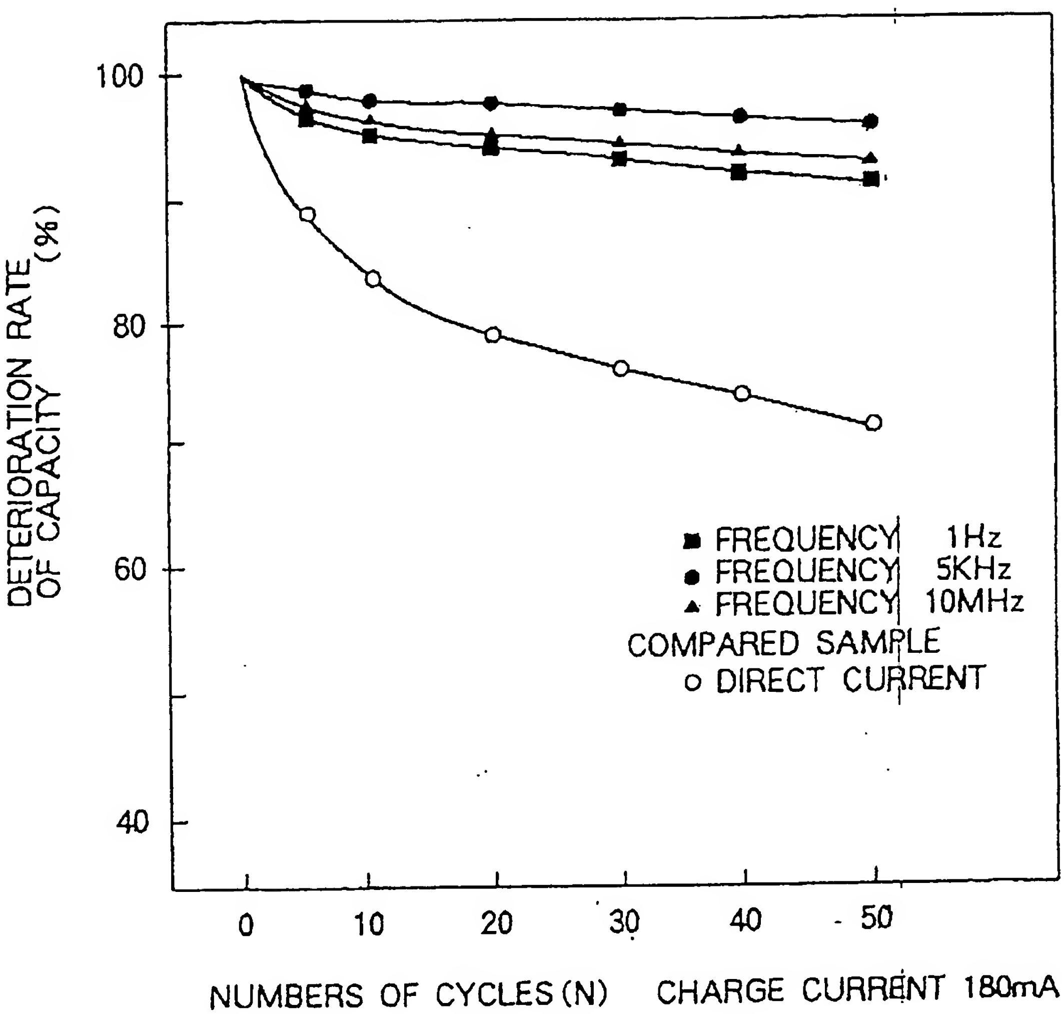

100
80
60
40
DETERIORATION RATE OF CAPACITY (%)
0
10
20
30
40
50
NUMBERS OF CYCLES (N)
CHARGE CURRENT 180mA
FREQUENCY 1Hz
FREQUENCY 5KHz
FREQUENCY 10MHz
COMPARED SAMPLE
DIRECT CURRENT

FIG. 11

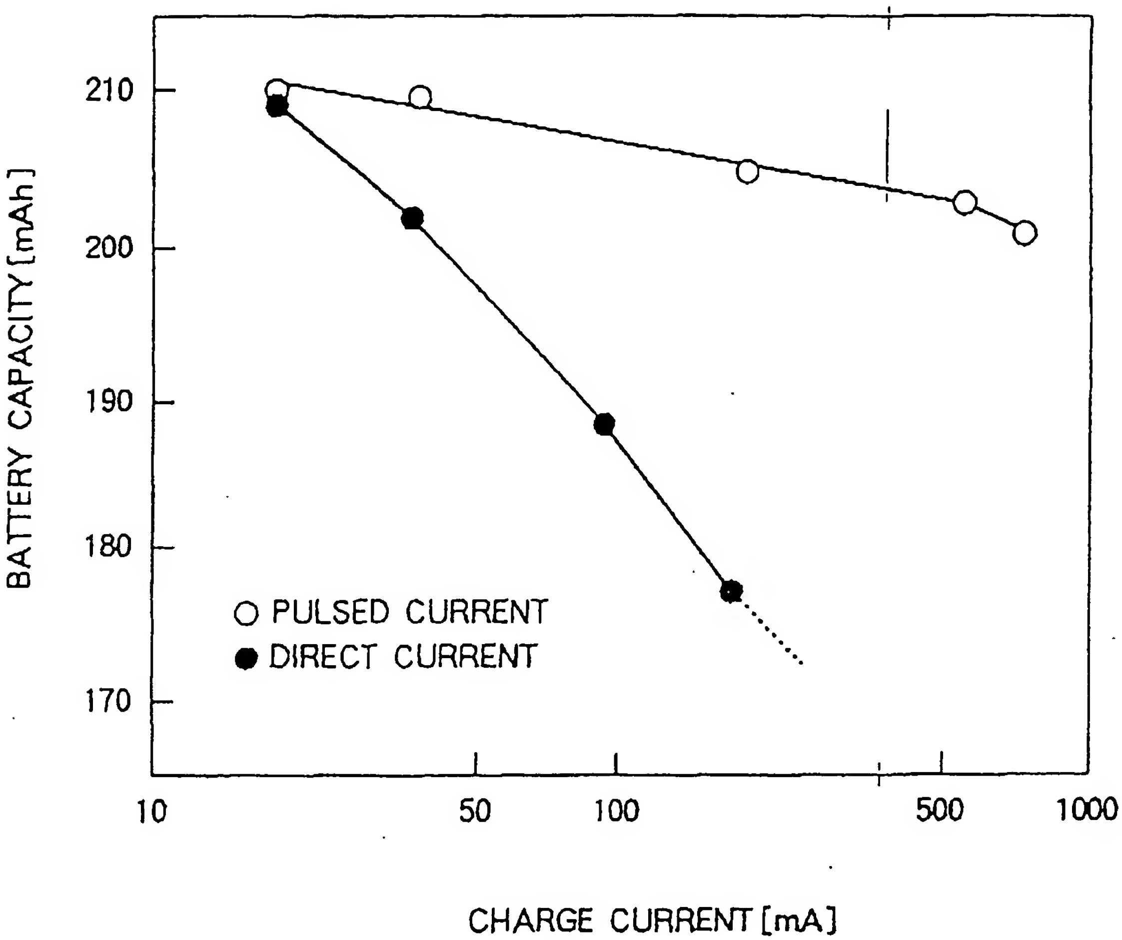
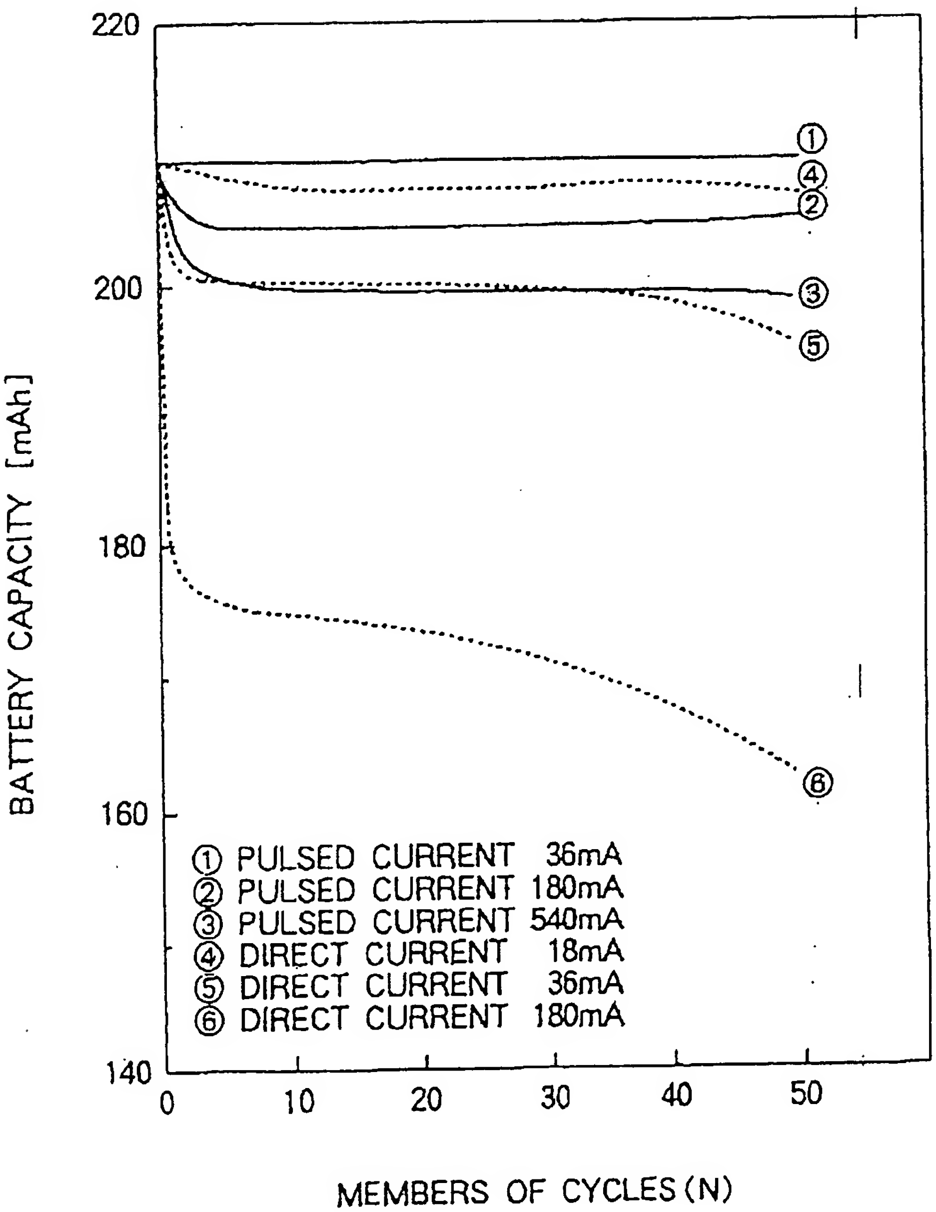

210
200
190
180
170
BATTERY CAPACITY [mAh]
10
50
100
500
1000
CHARGE CURRENT [mA]
PULSED CURRENT
DIRECT CURRENT

FIG. 12



220
200
180
160
140
BATTERY CAPACITY [mAh]
0
10
20
30
40
50
MEMBERS OF CYCLES (N)
①
④
②
③
⑤
⑥
① PULSED CURRENT 36mA
② PULSED CURRENT 180mA
③ PULSED CURRENT 540mA
④ DIRECT CURRENT 18mA
⑤ DIRECT CURRENT 36mA
⑥ DIRECT CURRENT 180mA

FIG. 13

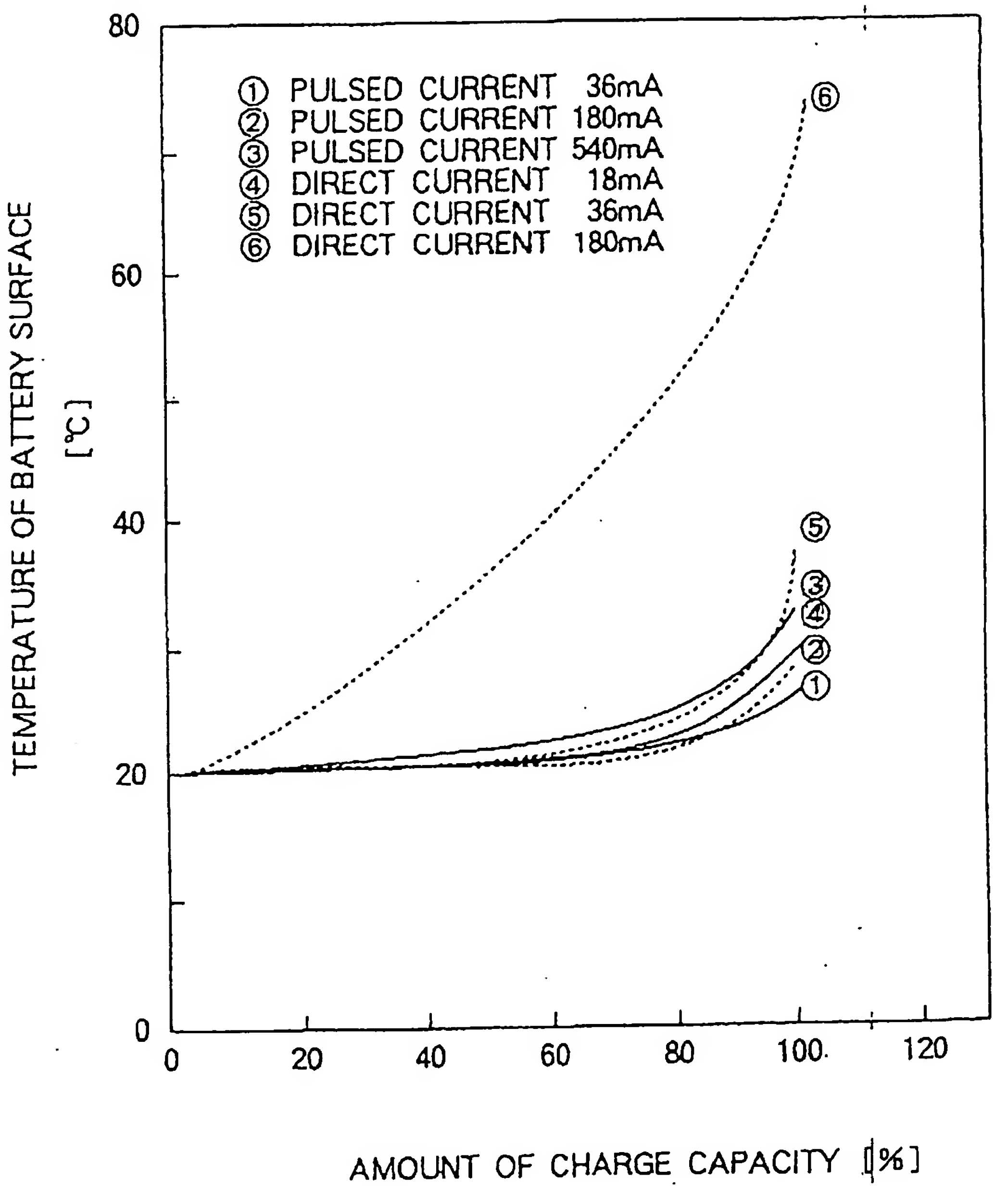

80
60
40
20
0
0
20
40
60
80
100
120
TEMPERATURE OF BATTERY SURFACE [℃]
AMOUNT OF CHARGE CAPACITY [%]
① PULSED CURRENT 36mA
② PULSED CURRENT 180mA
③ PULSED CURRENT 540mA
④ DIRECT CURRENT 18mA
⑤ DIRECT CURRENT 36mA
⑥ DIRECT CURRENT 180mA
①
②
③
④
⑤
⑥

FIG. 14

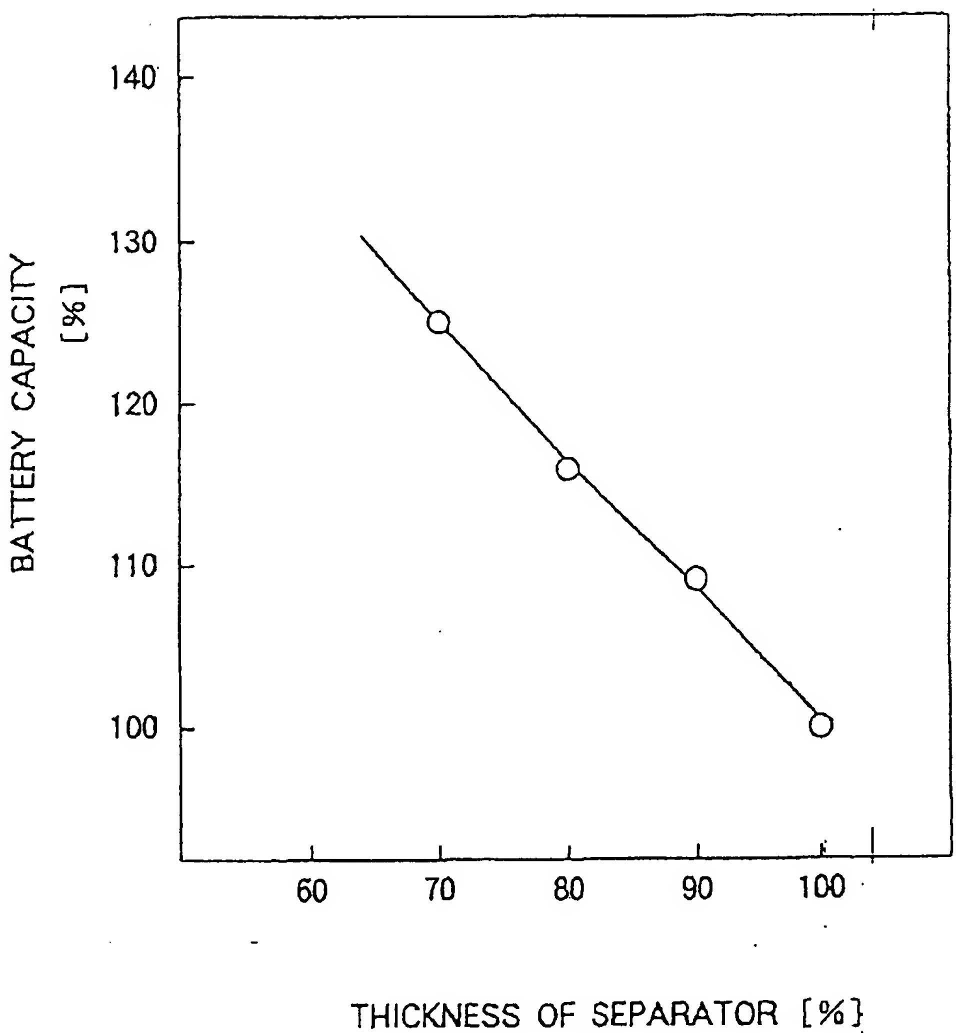
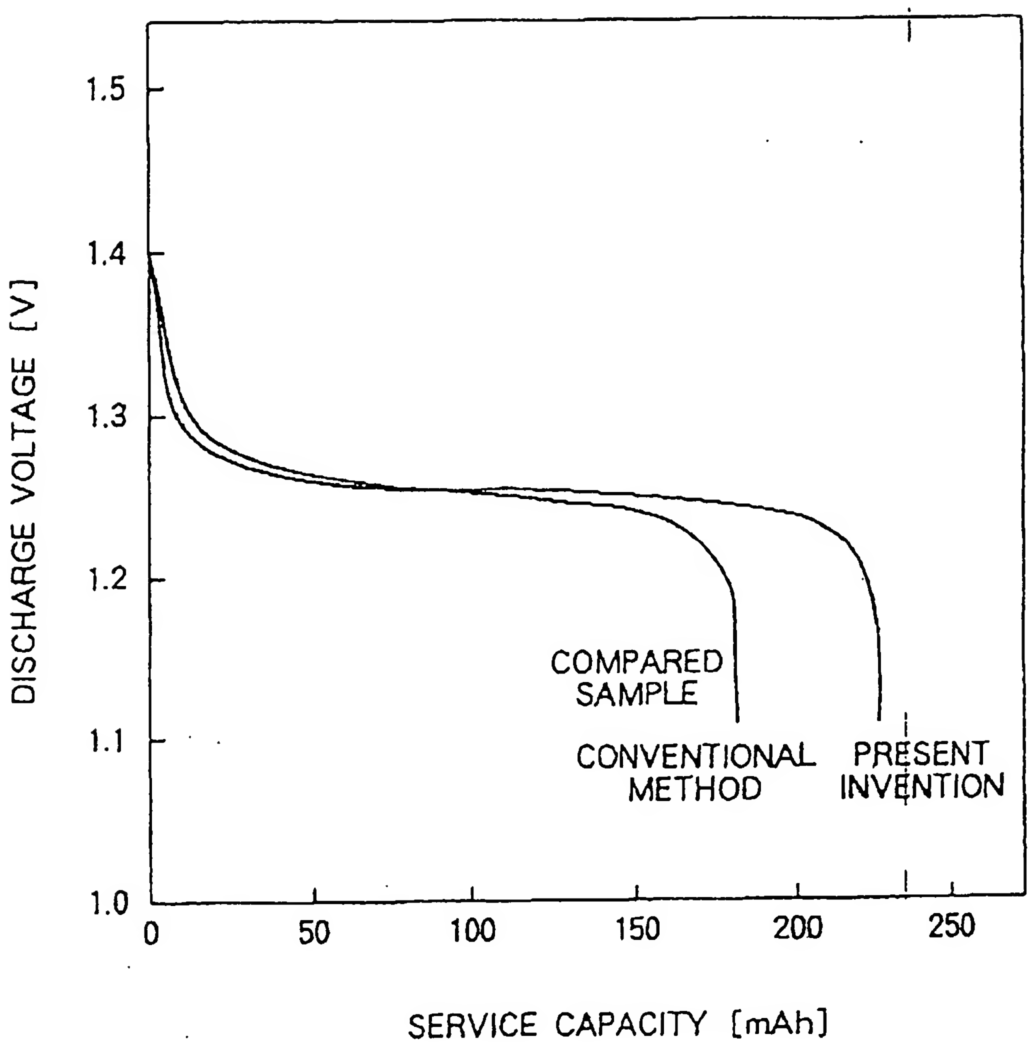

140
130
120
110
100
BATTERY CAPACITY [%]
60
70
80
90
100
THICKNESS OF SEPARATOR [%]

FIG. 15



1.5
1.4
1.3
1.2
1.1
1.0
DISCHARGE VOLTAGE [V]
COMPARED SAMPLE
CONVENTIONAL METHOD
PRESENT INVENTION
0
50
100
150
200
250
SERVICE CAPACITY [mAh]

FIG. 16

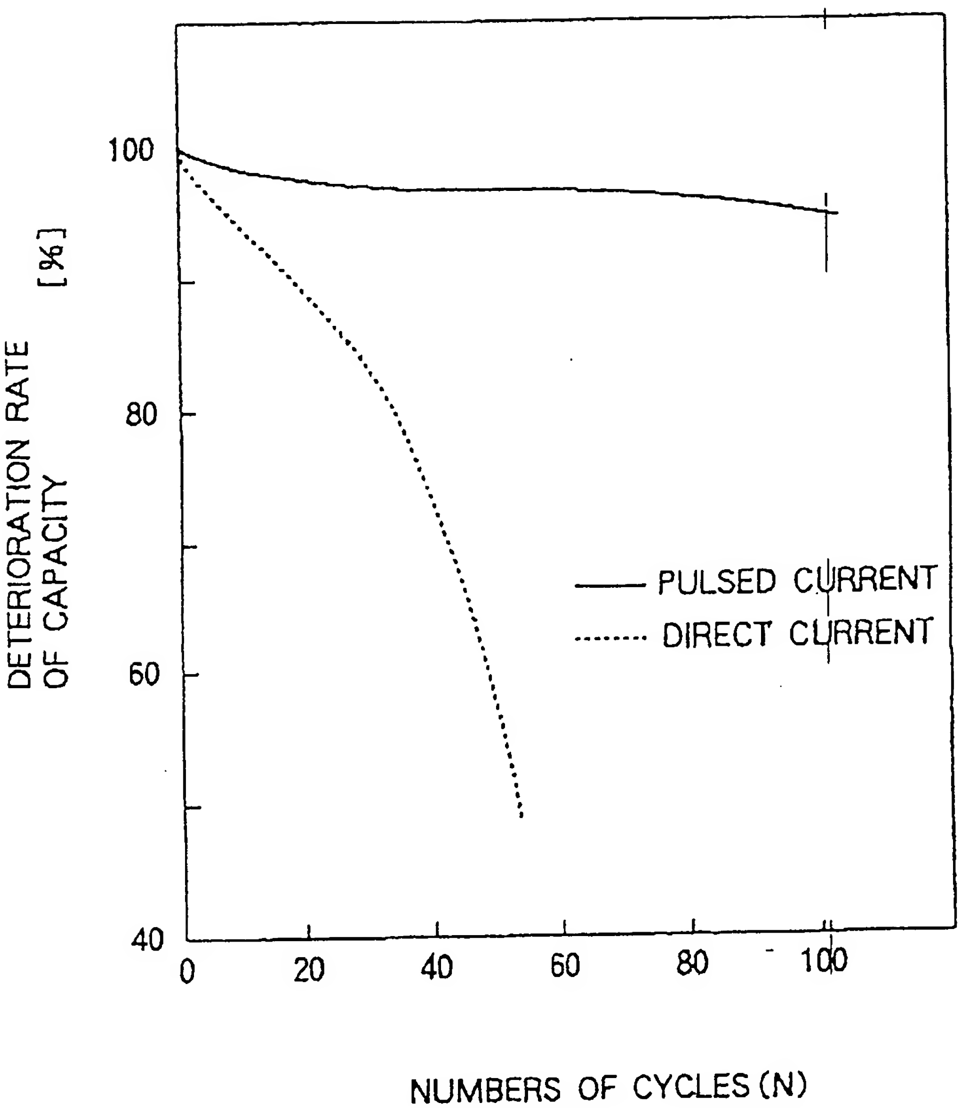

100
80
60
40
DETERIORATION RATE
OF CAPACITY
[%]
0
20
40
60
80
100
PULSED CURRENT
DIRECT CURRENT
NUMBERS OF CYCLES (N)

FIG. 17

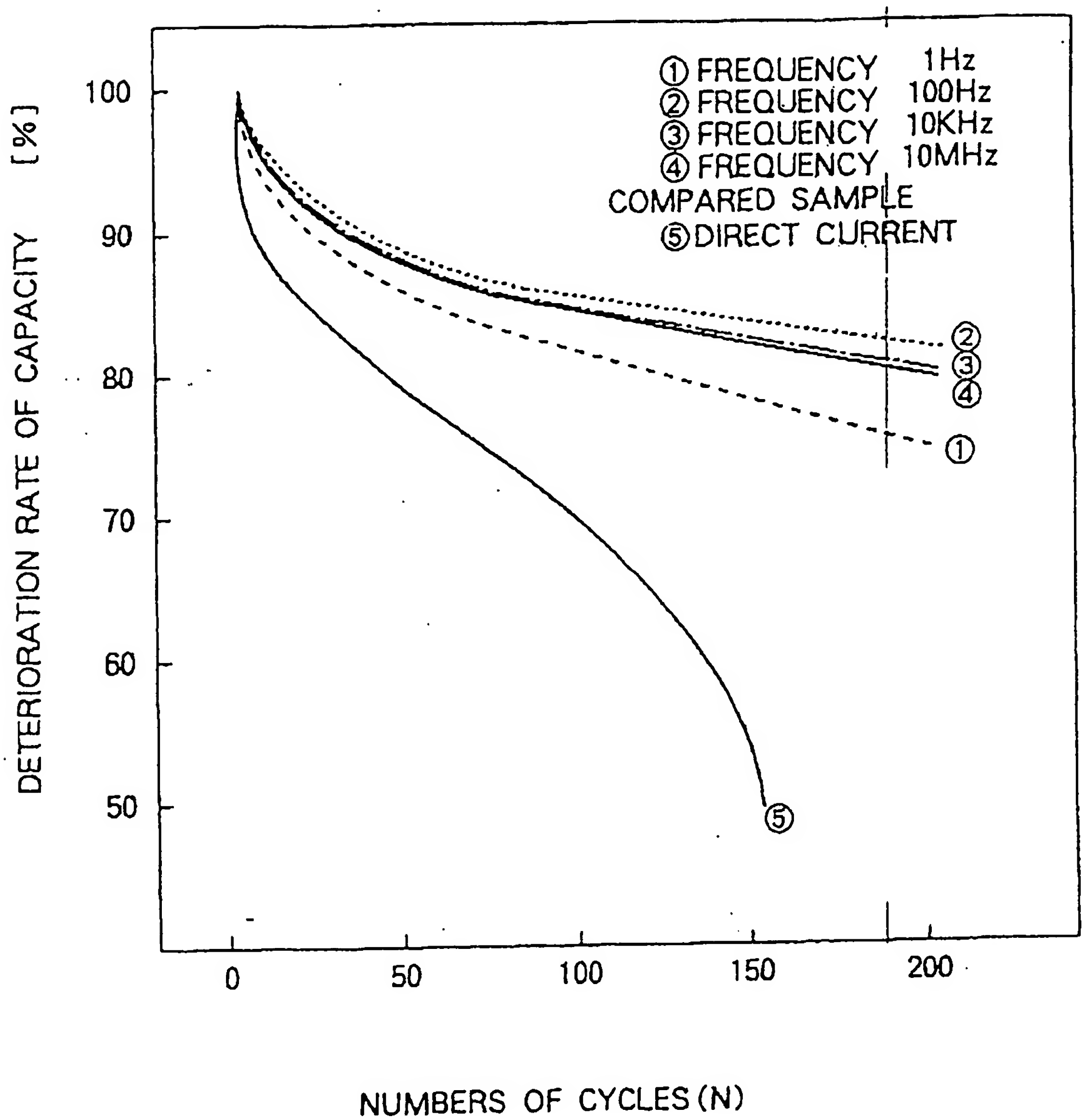
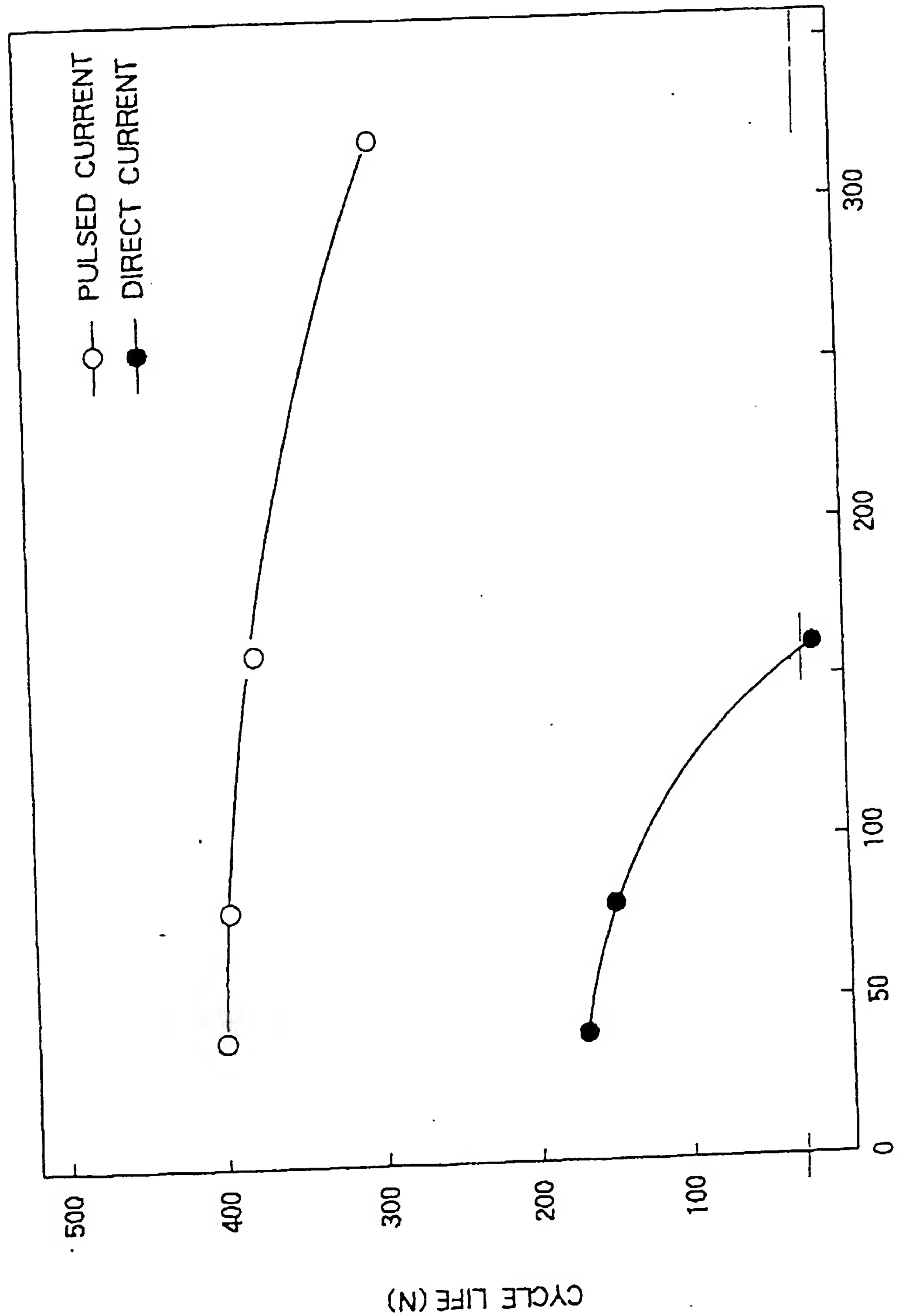

① FREQUENCY 1Hz
② FREQUENCY 100Hz
③ FREQUENCY 10KHz
④ FREQUENCY 10MHz
COMPARED SAMPLE
⑤ DIRECT CURRENT
DETERIORATION RATE OF CAPACITY [%]
100
90
80
70
60
50
0
50
100
150
200
NUMBERS OF CYCLES (N)
②
③
④
①
⑤

FIG. 18



PULSED CURRENT
DIRECT CURRENT
CYCLE LIFE (N)
500
400
300
200
100
0
50
100
200
300
CHARGE CURRENT [mA]

FIG. 19

A

(1)

FIG. 20(a)

20μm

(2)

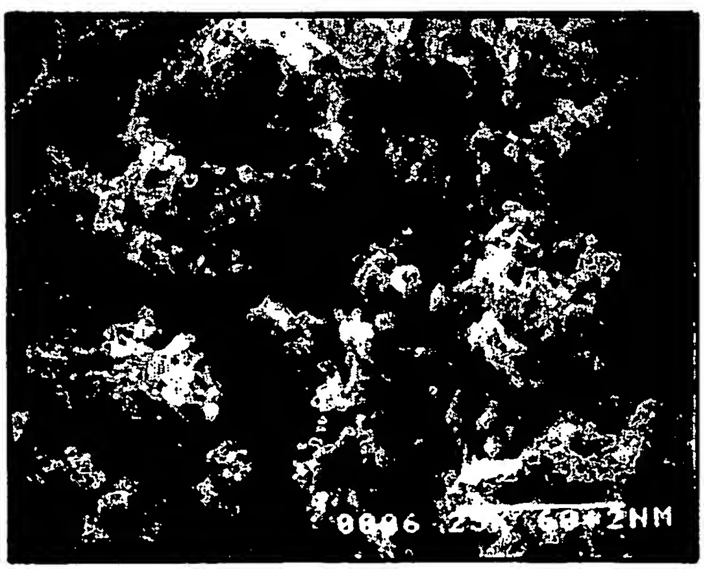


FIG. 20(b)

20μm